

## COOLING DEVICE FOR END-BOX OF MERCURY CATHODE CHLOR-ALKALI CELLS

### DESCRIPTION OF THE PRIOR ART

The production of chlorine by electrolysis of alkali chloride solutions, in particular of sodium chloride and potassium chloride (hereafter brine), is currently carried out by means of three different processes, respectively the ion-exchange membrane, the porous diaphragm and the mercury cathode ones. The latter type is based on a long-time known technology which has experienced a continuous improvement in the cell structure (Ullmann's Encyclopaedia of Industrial Chemistry, VCH, Vol. A6, page 416) essentially directed to the reduction of electrical energy consumption and to the lessening of mercury release in the environment.

The problem of the reduction of energy consumption has been successfully tackled by replacing the original graphite anodes with titanium anodes activated with a catalytic coating based on platinum group metal oxides which are also advantageously characterised by a long operative lifetime. This latter aspect allowed to substantially decrease the frequency of cell shut-downs imposed by the replacement procedures of graphite anodes, which were subject to a quite intense corrosion. Since the maintenance shut-down is critical in terms of mercury release in the environment, the benefit imparted by the activated titanium anodes is apparent also under this point of view. A reduction in the loss of mercury was further granted by the current employment of re-crystallised salt which allows minimising the amount of mercury-polluted sludges purged from the brine purification section, although involving a higher cost. Finally, a further decrease in the mercury release, particularly in the waters, was achieved by eliminating the demineralised water rinsing conventionally effected on the recycled mercury and on the amalgam respectively before entering the inlet end-box and after extraction from the outlet end-box. In this case the two end-boxes are known as dry end-boxes.

As a consequence of all these measures, it can be demonstrated at present that the release of mercury from a well designed and correctly managed plant does not exceed 1 gram/tonne of product chlorine versus the value of 10 grams of about ten

years ago (Ullmann's Encyclopaedia of Industrial Chemistry, VCH, Vol. A6, page 424).

Nevertheless, the adoption of dry end-boxes involves a quicker deterioration of the ebonite or of the vulcanised synthetic or natural rubbers commonly used as lining of the inlet end-boxes manufactured out of carbon steel. The observed problem originates by the relatively quick chemical attack of the lining as a consequence of the combination of the aggressiveness of fluids, in particular of chlorine, with the significantly higher temperature of the mercury which enters the cell at about 120°C; this temperature level directly derives from the lack of cooling consequent to the elimination of the rinsing with demineralised water and from the absence of external thermal exchange devices as preferred for the sake of installation simplicity. Furthermore an evident loss of adhesion to the underlying carbon steel occurs, with the consequence of making the start-up and shut-down thermal transients critical. To worsen the situation finally concurs the difficulty, not to say the impossibility, of repairing the damaged zones.

All of this forces the operators to perform shut-downs to proceed with replacing the deteriorated end-boxes with new ones every 3-4 years on the average. The replacement in its turn introduces an additional problem which makes the already expensive operation even more onerous: the lining of the disassembled end-box in fact contains non negligible amounts of highly toxic products such as dioxins and furanic compounds, generated by the reaction with chlorine at the cell operating temperatures. It follows a remarkable complication in the operations of detachment of the worn rubber and a considerable cost of disposal.

To overcome the problem, many different types of lining provided with higher chemical inertia and applied with different procedures have been proposed: one example is given in US 6,200,437, wherein the use of fluorinated polymers such as polyvinylidenefluoride (PVDF), polychlorotrifluoroethylene (PCTFE) and tetrafluoroethylene - hexafluoropropylene copolymer (FEP) is disclosed. However, the employment of the application procedures disclosed in US 6,200,437 is feasible, for instance, for lining the cell sidewalls, while it is practically not possible for the end-boxes because of the very complicated structure with the presence of several corners.

Entirely similar problems are presented by the end-boxes wholly made of plastic material, for instance polycyclopentadiene, commercialised under the trade-mark Telene<sup>®</sup> by BFGoodrich Co./USA, or other types of polymers optionally reinforced with glass fibres, aramidic fibres such as polyparaphenylen terephthalamide (commercialised as Kevlar<sup>®</sup> by DuPont/USA) or carbon fibres. Although marginally extended operative life-times can be obtained, in all cases not longer than 6-7 years, this solution is hardly appreciated by the plant operators as it involves substantially higher manufacturing costs and a certain design rigidity, due to the necessity of using moulds, which makes the introduction of subsequent improvements problematic.

The object of the invention is to overcome the constructive limitations of the cell inlet end-boxes of the prior art.

Under a first aspect the present invention is directed to a device capable of ensuring a much greater lifetime to the conventional end-box linings.

Under a second aspect the device of the invention ensures an extended operative lifetime by reducing the mercury temperature at the cell inlet.

Under a third aspect of the invention the device achieves the reduction of the recycled mercury temperature before entering the cell by a thermal exchange between the mercury and the feed brine effected inside the dry operating inlet end-box.

Under a fourth aspect of the invention the thermal exchange between mercury and feed brine is intensified by the dispersion of mercury into rivulets and/or droplets falling through the brine.

Under a fifth aspect of the invention the device constitutes a preassembled object which is installed inside new or used end-boxes independently from the design type or size.

Under a sixth aspect of the invention the device is easily repairable in case of accidental damages, in particular mechanical damages originated during the transport phase from the manufacturer to the user plant and during the phases of assembly in the cells and of plant general maintenance.

Finally, under a further aspect of the invention the inlet end-box equipped with the device allows minimising the temperature profile inside the cells with an improved

current density distribution.

## THE INVENTION

Under a first aspect, the invention consists of a dry-operating inlet end-box for mercury cathode chlor-alkali cell, provided with a conduit for feeding brine, a slit for the inlet of recycled mercury and a baffle for the generation of a mercury mobile film of predetermined thickness, further provided with an internal device for the thermal exchange between the brine feed and the recycled mercury. In a preferred embodiment, said internal thermal exchange device comprises an element deputed to the dispersion of the recycled mercury, for instance consisting of a distribution tank provided with holes or of a horizontal tray with lifted edge, and a second element deputed to the raising of the brine feed level, for instance a box provided with an overflow.

Under a second aspect, the invention consists of a mercury cathode chlor-alkali cell comprising a dry inlet end-box provided with an internal device for the thermal exchange between the brine feed and the recycled mercury.

Under a third aspect, the invention consists of a mercury cathode chlor-alkali electrolysis process carried out in the cell of the invention and characterised by a uniform longitudinal thermal distribution.

The invention will be described hereafter by resorting to the appended figures, which have a merely exemplifying function and do not wish to limit the scope thereof in any way.

## BRIEF DESCRIPTION OF THE DRAWINGS

- Figure 1: longitudinal section of a mercury cathode chlor-alkali electrolysis cell provided with a rinsing device with demineralised water effected before the inlet end-box and after the outlet end-box.
- Figure 2: front-view (A) and relevant cross-section along the line O – O (B) of a dry-operating inlet end-box.
- Figure 3: cross section of a dry-operating inlet end-box according to a first embodiment of the invention
- Figure 4: cross section of a dry-operating inlet end-box according to a second embodiment of the invention
- Figure 5: cross section of a dry-operating inlet end-box according to a third



embodiment of the invention

- Figure 6: cross section of a dry-operating inlet end-box according to a fourth embodiment of the invention

#### DETAILED DESCRIPTION OF THE DRAWINGS

In figure 1 it is sketched a conventional mercury cathode chlor-alkali cell section wherein (1) indicates the activated titanium anodes provided with catalytic film for chlorine evolution, (2) the cathode consisting of a layer of mercury flowing on the carbon steel bottom (dashed zone), (3) the brine feed, (4) the brine level inside the cell, (5) the decomposer where the amalgam forms, upon reacting with demineralised water, caustic soda or potash (6), hydrogen (7) and mercury (8) to be recycled to the cell through the pump (9), (10) the chlorine outlet, (11) and (12) the sections of rinsing of the recycled mercury before the inlet end-box (13) and of the amalgam downstream the outlet end-box (14). The terms inlet end-box and outlet end-box are intended as indicating the sections respectively connected to the initial part of cell, with the purpose of ensuring the uniform non-turbulent feeding of the sodium or potassium chloride solution and of the recycled mercury, and to the terminal part of the cell for the separation of the sodium amalgam from the chlorine-containing diluted brine.

For a better understanding of the invention it is convenient to describe the functioning of the conventional dry inlet end-box sketched in figure 2 as front-view (A) and as cross-section along the line O-O (B), wherein (15) indicates the conduit for feeding brine at about 60°C (8-18 m<sup>3</sup>/hour depending on the current density and on the cell size), (16) a cylindrical horizontal distributor provided with perforations along the lower generatrix through which the brine percolates, (17) the brine level (uniform dashed line), (18) the gaseous atmosphere essentially consisting of chlorine and water vapour, (19) the slit for the recycled mercury inlet at about 120°C coming from the circuit of the decomposer (4-8 m<sup>3</sup>/hour depending on the current density and on the cell size), (20) the level of mercury (dashed and dotted line), (21) a baffle allowing to introduce a mobile layer of mercury of predetermined thickness into the cell (22) through the passage (23), (24) the end-box body of carbon steel lined with a continuous sheet of vulcanised rubber.

The mercury and brine flows indicated by the arrows of figure 2 are substantially of

the laminar type and are characterised by very reduced contact times which do not allow to achieve any significant thermal exchange: in fact, temperatures of brine (34) and mercury (35) were determined in correspondence of the inlet of cell (22) different by only 4-5°C with respect to the feed values.

With the above indicated operating conditions the rubber, inspected after one year of functioning, results in general already characterised by a powdery appearance extended to the whole surface and by a corrosion in form of an about 1 mm deep groove approximately in correspondence of the level of mercury. The powdery appearance is attributable to the reaction with the chlorine in the gaseous atmosphere, the groove formation to the presence of substantial amounts of hypochlorite and chlorate in the liquid film present in the interstice formed by the mercury meniscus against the rubber wall.

The industrial experience indicates that the chemical reactions at the basis of the described types of deterioration are very sensible to temperature, in particular when the latter exceeds the critical level of 90-95°C.

Starting from this basis of knowledge the inventors have studied the efficiency of modifications in the design of inlet end-boxes with the main purpose of decreasing the temperature of mercury at the cell inlet point. In particular, the internal thermal exchange devices illustrated in the following have been considered, suitable for being installed on the existing or newly manufactured inlet end-boxes independently from the model type and size and consisting of a first element for the dispersion of the recycled mercury and preferably by a second element for raising the brine level:

- inlet end-box A, illustrated in figure 3, provided only with the first element consisting of a horizontal cylindrical distributor connected to one of the sidewalls and perforated along the lower generatrix for the distribution of mercury, identified with (25). In the figure an end-box section is sketched in which the slit (19) is sealed with a bolted sheet provided with a perimetrical sealing gasket. The other constituent parts of the end-box were entirely equivalent to those already identified in figure 2.
- inlet end-box B, illustrated in figure 4, equivalent to end-box A and further equipped with the second element consisting of a case (26) directed to

establish, through the overflow (27), a new brine level (28) with the purpose of increasing the thermal exchange with mercury. The case (26) was further provided with a damper (29) of the kinetic energy of the brine falling from the overflow (27), with the purpose of preventing undesired turbulences of the mercury layer.

- inlet end-box C, illustrated in figure 5, equivalent to end-box B, but equipped with the first element comprising a horizontal tray (30) provided with a lifted edge, installed inside the case (26) and in particular below the brine level (28). The lifted edge was provided with a multiplicity of upper openings (31), having a triangular passage section (in less preferred embodiments of the invention the lifted edge may also be free of openings or the opening passage section may also have a different geometric shape, for instance rectangular). The multiplicity of openings was directed to achieve a mercury flow dispersion into a multiplicity of rivulets and droplets. The mercury feed to the tray was again realised with a perforated horizontal cylindrical distributor (25) secured to the sidewall of the end-box with the slit (19) sealed. Alternatively it is possible to resort, for the feeding of mercury, to a vertical pipe connected through an appropriate connection to the feed slit (19) which in this case is obviously not sealed, or to a coaxial pipe internal to the brine feed conduit (15), with the slit (19) also in this case sealed. The latter solution is particularly interesting for its constructive simplicity, however with the disadvantage of introducing a higher hydraulic head on the circulation of mercury, with for certain types of pumps (element (9) in figure 1) may lead to lower flow-rates.
- inlet end-box D, illustrated in figure 6, equivalent to type C, but with the tray edge provided with a double multiplicity of upper and lower openings (31) with triangle-shaped sections.

The cases (26) of end-boxes B, C and D directed to raise the brine level were provided of one or more ducts (32) on the back-wall, for discharging the mercury which established a level (33) in their interior, so as to oblige the brine to pour out above the overflows (27).

The perforated distributors (25), the trays (30) with the relevant edges, the boxes (26) and the connecting tubes were made of titanium and preferably maintained

electrically insulated from the carbon steel of the end-boxes. It is evident that, given the simplicity of the design, these elements may as well be constructed with other materials, provided they resist to the harsh operating conditions typical of chlor-alkali cells: for example, one may suppose resorting to polymeric materials such as the aforementioned Telene<sup>®</sup> or even better to easily mouldable and weldable polymeric perfluorinated materials, such as PVDF, FEP, PCTFE. The ducts (32) were manufactured with polytetrafluoroethylene (PTFE) tube. Metal ducts are also acceptable provided they are lined with electrically insulating material.

End-boxes A, B, C and D, internally provided with rubber commercialised under the trade-mark Akorros<sup>®</sup> CS 1710 by A. Tamburini & C. S.r.l./Italy, were installed each on a cell of a mercury cathode chlor-alkali electrolysis industrial circuit characterised by the following features:

- Brine fed at about 60°C with average flow-rate of 8 m<sup>3</sup>/hour/cell
- Mercury fed at about 120°C with average flow-rate of 4 m<sup>3</sup>/hour/cell
- Operative current: 180 kA/cell, corresponding to a density of 12 kA/m<sup>2</sup>
- Anodes of activated titanium, provided with ruthenium-iridium-titanium mixed oxide-based catalytic coating
- Thermocouples inserted in each of the four test cells and in particular in the brine at the cell inlet (indicated as (34) in figure 3), in the mercury immediately downstream passage (23) (indicated as (35) in figure 3), and in the mercury admission and brine feed conduits.

Before starting the operation, the hydraulic behaviour was checked by supplying mercury and brine at the above indicated flow-rates to each of the four still opened cells. In particular, it was observed that the fall of mercury from the perforations of the distributing pipe (25) of end-boxes A and B occurred in form of almost continuous and relatively coarse rivulets, while in the case of end-box C the same fall appeared as a rather fine dispersion of rivulets and droplets, even though with a certain tendency to coalesce in coarser rivulets; finally, in the case of end-box D the mercury fall appeared as a stable dispersion of fine rivulets and droplets.

The four cells were then started up and after a period of a few days of stabilisation, temperatures were detected through the various thermocouples installed, with the



following results:

- Cell equipped with end-box A - Temperature of mercury in the admission conduit: 120°C and in (35): 116°C, temperature of brine in the feed conduit: 60°C and in (34): 62°C, temperature of brine at the cell outlet: 90°C
- Cell equipped with end-box B - Temperature of mercury in the admission conduit: 119°C and in (35): 99°C, temperature of brine in the feed conduit: 60°C and in (34): 70°C, temperature of brine at the cell outlet: 89°C
- Cell equipped with end-box C - Temperature of mercury in the admission conduit: 118°C and in (35): 90°C, temperature of brine in the feed conduit: 60°C and in (34): 74°C, temperature of brine at the cell outlet: 88°C
- Cell equipped with end-box D - Temperature of mercury in the admission conduit: 122°C and in (35): 90°C, temperature of brine in the feed conduit: 60°C and in (34): 76°C, temperature of brine at the cell outlet: 91°C

After 13 months of operation the functioning of the four cells was stopped and the conditions of the inlet end-box lining were checked.

End-box A showed the superficial powdery aspect commonly observed with the conventional dry inlet end-boxes operating with mercury at temperatures substantially higher than 90°C and the characteristic groove, in this case about 1.5 millimetre deep, along the end-box periphery in the meniscus zone between mercury and sidewall. This state of conservation allowed foreseeing a residual life slightly higher than 2 years.

End-box B resulted to be affected by a totally marginal powdering, while the perimetrical groove was reduced to a simple band of different colour from the surrounding surface. In principle for this end-box an operating lifetime certainly superior to the average duration of 3 years, typical of the conventional dry inlet end-boxes, can be foreseen.

End-box C looked very well preserved, with no significant traces of powdering and with only a slight discontinuous band with a different colouring from that of the surrounding material, while end-box D appeared practically unvaried to a visual survey with respect to the situation of the first start-up. For both of the end-boxes C and D a much higher lifetime could thus be foretold than the average duration of 3 years of the conventional dry inlet end-boxes.

The positive result observed with the testing of end-boxes B and especially C and D is attributable beyond any doubt to the strong reduction in the temperature of the mercury coming in contact with the lining. The temperature reduction is in its turn due to the much more efficient thermal exchange between mercury and brine feed within the device of the invention. In particular, the higher efficiency is the result of the concurrence between the splitting of mercury in a particularly stable fine dispersion in the case of end-box D and the higher level of brine through which the mercury dispersion falls, with the overall consequence of an increase both of the contact time and of the heat exchange surface. The thermal exchange is especially effective with the adoption of the tray with edge provided with a multiplicity of openings of end-box C and even more with the kind of tray of end-box D characterised by a double multiplicity of openings which, as seen, stabilises the dispersion of falling mercury.

The disappointing result of end-box A is evidently caused by the lack of one of the two factors of success of end-boxes B, C and D: in end-box A, in fact, where the device of the invention is reduced to the distributing perforated pipe alone, the brine level is rather low as happens in the conventional inlet end-boxes and therefore the contact time of mercury with brine is much limited. It follows a modest heat exchange which diminishes only marginally the mercury temperature. A side advantage of the invention, particularly when practised by employing end-boxes of type B, C and D, is given by the temperature levels at which mercury and brine enter the cell: these levels allow achieving a temperature longitudinal distribution along the cell much more uniform than what occurs in the cells equipped with the conventional inlet end-boxes. The moderate temperature profile reflects in its turn on a physiologically better current density distribution, and hence on an easier automated regulation of the functioning with a prolongation of the anode average duration.